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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup> : <b>H01L 31/04 // H01G 9/20, H01M 14/00</b>		A1	(11) International Publication Number: <b>WO 99/63599</b>
			(43) International Publication Date: 9 December 1999 (09.12.99)
(21) International Application Number: PCT/SE99/00290		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).	
(22) International Filing Date: 1 March 1999 (01.03.99)		Published <i>With international search report. In English translation (filed in Swedish).</i>	
(30) Priority Data: 9801799-9 20 May 1998 (20.05.98) SE			
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(54) Title: DYE SENSITIZED NANO-STRUCTURED PHOTO-VOLTAIC TANDEM CELL			
(57) Abstract			
<p>The invention provides a device for obtaining an improved efficiency in a photo-voltaic, nano-structured, dye sensitized cell structure, comprising a photo-active working electrode (WE1), a counter electrode (WE2) and an electrolyte (5) arranged therebetween. The cell structure thereby forms a tandem cell in that the counter electrode also is a photo-active electrode, whereby the photo-active working electrode and/or the photo-active electrode are built on a transparent substrate. Furthermore, both the photo-active working electrode and the photo-active electrode are made of porous nano-structured film and the photo-active working electrode is dye sensitized with a first dye (Dye1). The first dye is selected such that the electron injection into the working electrode is so fast that the red-form of a redox-couple in the electrolyte as fast as possible replaces an injected electron. The second dye (Dye2) is selected such that it has a long lived excited state. In this case the material in the counter electrode is comprised of a semi-conductor having a large band-gap. In an alternative embodiment, the working electrode is dye sensitized corresponding to the first embodiment, whereas the counter electrode is comprised of a semi-conductor with a band-gap having absorption in the visible and/or infra red region, whereby the light absorption in this electrode is further enhanced by a dye having been adsorbed onto the surface of said electrode.</p>			

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## DYE SENSITIZED NANO-STRUCTURED PHOTO-VOLTAIC TANDEM CELL

The present invention relates to a photo-voltaic cell, in particular one having a cell structure comprising two electrodes with an electrolyte located there between, and where at least one of the electrodes has an active surface in the form of a dye sensitized nano-structured film.

### Background of the Invention

Photo-voltaic cell, commonly referred to as solar cells, have a potential of having a breakthrough on the energy market for the generation of electricity directly from the sun light.

The critical factor will be the cost at which the energy generated by the sun can be produced.

During the entire post-war era the solar cell technology has been developed and the cost per kWh has been reduced. Solar cells at prices accepted by the market for the production of electricity are today available only in special fields of use. For a more general utilization of electrical power produced by solar cells, cheaper and more efficient solar cells are required.

The traditional solar cells are based on either a Schottky-barrier between a metal and a semi-conductor, or on a so called p-n junction in one and the same semi-conductor material. A photo-voltage and a current is generated on illumination of the Schottky-barrier or the p-n junction alternatively. The early variants of such cells were based on crystalline materials.

High purity was necessary in order to achieve a high efficiency. However, crystalline systems become expensive and they can today for economic reasons not be employed in large scale generation of electrical power. To overcome this problem a number of different solar cells have been developed in thin film technology. The most well known and promising cells are constructed from amorphous silicon. The amorphous silicon solar cells have been possible to

handle by creating cells made up of several thin layers, doped as p-i-n, where "i" stands for intrinsic (undoped) layer. By stacking several, up to three, p-i-n structures above each other better stability as well as higher efficiency have been achieved. After an initial period of deterioration, the efficiency stabilizes around 10%. Another route to high efficiency is offered by thin films of binary or ternary, highly absorbing chalcogenides, usually selenides and tellurides, e.g. cadmium selenide (CdSe), cadmium telluride (CdTe) and copper indium di-

selenide ( $\text{CuInSe}_2$ ). The cadmium compounds are questioned, but  $\text{CuInSe}_2$  cells, often referred to as CIS cells, are regarded as promising. Sometimes they have gallium added in order to optimize the band gap, and are then referred to as (CIGS). For the optimization of the efficiency the CIS and CIGS are provided with a thin layer of cadmium sulfide (CdS). Cells of this type can have efficiencies of up to 17% under 1,0 sun (AM 1). Modules having up to

12% sun light efficiency have been built. The technology is developing. Attempts are made to eliminate the CdS layer, which is environmentally less desirable.

A new line of development in the context of solar cells, is the nano-structured, dye-sensitized solar cells. Often the abbreviation DSC is used (Dye Sensitized Solar cell). The development of DSC gained momentum in the early 90's, primarily by the efforts made by M. Grätzel at EPFL in Lausanne, Switzerland (see EP-A-0 333 641, WO 95/18456, US-A-5,350,644, US-A-5,525,544, US-A-5,441,827, alla Grätzel et al). Cells of this type are known since the late 70's, when they were studied e.g. by a number of Japanese researcher. The function of DSC differs significantly from the classical Schottky-barrier cells with junction of the p-n or p-i-n type. Such a cell comprises a working electrode, an electrolyte and a counter electrode. The working electrode is sensitized with a dye, to render it photo-active in the visible spectrum (sun light).

This dye sensitized, nano-porous, nano-crystalline (or nano-structured) thin film solar cell, presented by O'Reagan and Grätzel in Nature 1991, thus has a photo-active anode and a passive cathode, only serving to in an efficient way regenerate the redox-species that is oxidized at the sensitized, nano-structured photo anode.

This type of cell usually reaches cell efficiencies of 6-9%, although 11% has been reported. The upper theoretical limit is about 30%.

A possibility to increase the efficiency would be to combine the Grätzel/O'Reagan cell with a photo-active cathode of a p-type poly-crystalline or single-crystalline semi-conductor, with a low band-gap. Example thereof could be p-CdSe, p-CdTe, p-InP etc. However, these semi-conductors are unstable in most electrolytes.

On illumination a photo-voltage may be registered at the terminal connections of the cell, and if the circuit is closed with an external lead, an electrical work can be performed externally of the cell. The maximum value of the photo-voltage,  $U_{OC}$ , is the difference between the energy level of the redox couple in the solution, and the level of the conduction band. The photo-current will be directly dependent on the number of absorbed photons, resulting in the injection of electrons in the conduction band, and on any losses of electrons back to the electrolyte, which take place during the transport thereof towards the back contact. The primary drawback with prior art solar cells, briefly described above, is in practice their low

- efficiency. Thus, there is a desire for further developments and improvements of the existing technology in order to achieve better and more efficient solar cells, for enabling to a greater extent the utilization thereof within the continuously growing field of electronic equipment.

## 5 Summary of the Invention

The object of the invention is to provide a thin film solar cell having a higher photo voltage, and thereby a higher efficiency. This is achieved by a dye sensitized solar cell of the tandem type, wherein both the anode and the cathode are photo-active and wherein at least one 10 electrode, preferably both, are dye sensitized. The invention is defined in claim 1.

The theoretical efficiency for this cell is about 45%.

For the case wherein both electrodes are dye sensitized, the valence band of the photo-active 15 cathode is at an energy level which is above the HOMO level (Highest Occupied Molecular Orbital) for the dye with which the cathode has been sensitized.

The conduction band of the anode lies at a level which is below the LUMO level (Lowest Occupied Molecular Orbital) for the dye with which the anode has been sensitized.

20 Furthermore, the HOMO level of the dye for the anode is lower than the level of the redox-couple, and the LUMO level of the cathode is higher than the level of the redox-couple. The cell structure according to the present invention thereby forms a tandem cell, in that the counter electrode also constitutes a photo-active electrode, whereby the photo-active working 25 electrode and/or the photo-active electrode is made up on a transparent substrate. Also, both the photo-active working electrode and the photo-active electrode comprise porous, nano-structured film. In one embodiment the photo-active electrodes are dye sensitized with a first and a second dye, respectively. The first dye is selected such that the electron injection into the working electrode is so fast, that the red-form of a redox-couple in the electrolyte, as fast 30 as possible replaces an injected electron. The other dye is selected to have a long lived excited state. In this case the material in the counter electrode is a semi-conductor having a large band-gap. In a second embodiment the working electrode is dye sensitized, corresponding to the first embodiment, whereas the counter electrode comprises a semi-conductor having a band-gap absorbing in the visible and/or infrared range, whereby the light absorption in this 35 electrode is further enhanced by a dye, absorbed onto the surface of said electrode.

Embodiments of the invention are defined in claims 2-16.

### Brief Description of the Drawings

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The invention will be illustrated with reference to drawings in the form of a number of figures, wherein

10 Figure 1 shows a cross section through a prior art sandwich cell of the DSC type,

Figure 2a shows a cross section through a DSC, which also shows, on a vertical scale, the energetic relations between semi-conductor, dye and electrolyte,

15 Figure 2b shows schematically the spectral light absorption for the dye and the semi-conductor material in the prior art DSC type,

Figure 3 shows a cross section through a prototype of a sandwich cell of the TDSC type in accordance with the invention,

20 Figure 4a shows another cross section through TDSC according to the invention, showing on the vertical scale the energetic relations between semi-conductor, dye and electrolyte,

Figure 4b shows schematically the spectral light absorption in the first and second dye respectively, and in the semi-conductor materials for the embodiment disclosed in Figure 4a,

25

Figure 5a shows cross section through a further embodiment a TDSC in accordance with the invention,

30 Figure 5b shows schematically the spectral light absorption in the first and second dye respectively, and in the semi-conductor materials for the embodiment disclosed in Figure 5a,

Figure 6 shows iV characteristics for a dye sensitized NiO electrode in three electrode set-up vs Ag/AgCl electrode,

35 Figure 7a shows iV characteristics of a dye sensitized TiO<sub>2</sub> electrode,

Figure 7b shows iV characteristics of a dye sensitized NiO electrode,

Figure 7c shows iV characteristics of a tandem cell comprising a dye sensitized TiO<sub>2</sub> electrode and a dye sensitized NiO electrode.

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### Description of Preferred Embodiments

Figure 1 shows schematically the design of a DSC. There are three essential components in such a DSC, a working electrode WE, an electrolyte 5 and a counter electrode CE. The 10 working electrode e.g. comprises transparent carrier substrate 1 made of glass or plastics, having a transparent thin film back contact 2, made e.g. of SnO<sub>2</sub>(F). The thin film (of the order 1-10 µm) comprises sintered oxide particles 3 covered by a mono-layer of a dye 4. The electrolyte 5 comprises a redox-system with suitable redox-couples. The counter electrode CE comprises a catalytic layer 8 on a transparent or opaque conducting film 9 on glass 10 or on 15 an opaque conducting substrate. The most efficient redox-system used today is the iodine/iodide system. The redox-system performs the charge transport between the two electrodes. One of the electrodes, which is a passive electrode, is here referred to as the counter electrode CE. The active electrode WE is constructed of a film, typically 5-10 µm thick, of a so called nano-structured material, i.e. a porous material of particles having 20 dimensions in the nanometer range.

The particles are sintered together to a solid film (if the material is comprised of nano-rods the rods may preferably be oriented perpendicularly against the underlying film, with the same dimension as the film thickness). It is essential that the cross section at right angles to the film 25 will have a very large internal surface. The film is located on a conducting transparent substrate, e.g. of SnO<sub>2</sub>(f), ITO or the like, which in its turn is located on a transparent carrier material, e.g. glass or plastics. For achieving efficient current collection, a metal mesh can be place under, in or on the conducting transparent film. The nano-structure in the active film can be comprised of a semi-conductor or an insulator, e.g. an oxide having a large band-gap. 30 A common oxide in this connection is TiO<sub>2</sub>. The oxide particles (or rods) are sintered together to a porous matrix.

The porosity is typically about 50%, which means that the electrolyte can penetrate the thin film all the way up to the conducting back contact. If the above mentioned oxide films are 35 used, they will normally have their absorption in the UV range and cannot by themselves

catch any larger portion of the sun light. However, if the surface of the particles (rods) are dyed with a dye having its absorption in the visible part of the solar spectrum, the efficiency can be improved substantially. A DSC is obtained. DSC prototypes having efficiencies of up to 1% have been made in this way (see Grätzel). The reason that the cell works is i.a. that the inner surface of the nano-structured thin film on the active electrode is very large, typically 1000 times larger than the geometrically illuminated surface. Even a single mono-layer of dye molecules, sticking to the inner surface of the film, yields such a strong dying of the inner surfaces, that the dye will absorb the major part of the light around its absorption maximum. Thereby the number of photons that can be absorbed in the visible spectral range increases, and thus also the efficiency.

Figure 2a shows in an energy diagram how the dye sensitized cell works energetically, and figure 2b shows schematically the spectral light absorption of the dye and the semi-conductor material SC1, respectively, in the described prior art DSC. In Figure 2a the left hand vertical axis corresponds to energy ( $E/eV$ ), which can also be expressed as a potential ( $V$ ) according to the right hand axis. In the working electrode WE, SC1 indicates the nano-structured porous semi-conductor oxide, with the levels of the valence band VB and the conduction band CB inserted. Furthermore, the energy level of the dye Dye 1 is inserted. It is essential that the conduction band CB of the semi-conductor film is below the lowest unoccupied electronic energy level, LUMO, of the dye. Also, it is important that the energy level Ured/ox of the redox-couple energetically is above the highest occupied electron energy level HOMO. This is required in order to obtain a driving force for the electron transitions.

A complete cycle for the motion of an electron through the cell will be as follows: upon photon excitation electrons will be lifted from the HOMO level of the dye to its LUMO level. The electrons in the LUMO level of the dye are injected into the conduction band of the oxide film, an extremely fast process with a half life of less than 100 femtoseconds. Therefrom they can pass out through the back contact and through an external lead transferred to the CE. This can be a relatively slow process with transit times in the millisecond range. At the CE they are received by the oxidized form (Ox) of the redox-couple which is in the electrolyte. Thereby the Ox is reduced and the red-form (Red) is obtained. Red moves, primarily by diffusion, through the electrolyte and returns the electrons to the photo-oxidized dye molecules. The electron cycle in the cell is thereby closed and a new can begin.

Figures 3-5 illustrate the principle of a dye sensitized tandem cell TDSC in accordance with the present invention. Figure 3 shows a cross section through a basic prototype of a sandwich cell of the TDSC type. In such a TDSC at least one electrode WE1 or WE2 is built on a transparent substrate having a conducting transparent film. The figure shows a TDSC where 5 both electrodes have transparent substrates with a conducting transparent film.

Thus, in Figure 3 the counter electrode in the simple dye sensitized cell (see Figure 1) has been replaced by a photo-active electrode, WE2. WE1 as well as WE2 thus are photo-active. This contributes to increase the cell efficiency. At least one of the electrodes is dye sensitized 10 and built up of a porous, nano-structured film. This electrode will be designated WE1 below. The function of WE1 is identical to what has been disclosed above for WE of Figure 1. It is dye sensitized by a first dye. Thus, in a TDSC at least one electrode, WE1 or WE2, are built on a transparent substrate having a conducting transparent film. If one of the electrodes is built on a transparent substrate with a conducting transparent film, sun light will impinge first 15 on this electrode.

In Figure 4a there is shown a cross section through a TDSC in accordance with the invention. Figure 4a shows on its vertical scale the energetic relations between semi-conductor, dye and electrolyte, all at the same time. On the left hand there is an axis for an energy scale (E/eV) 20 and on the right hand an axis for a potential scale (V/Volts). For the working electrode, SC1 is the nano-structured porous semi-conductor oxide, with the levels of the valence band VB and the conduction band CB inserted. Furthermore, the energy levels of the first dye, Dye 1, are inserted whereby HOMO 1 represents the lower level and LUMO 1 represents the higher level.

25 In the electrolyte, Ered/Ox indicates the energy level of the redox-system. For the working electrode WE2, SC2 is a nano-structured porous semi-conductor oxide with a large band-gap, and with the levels of the valence band VE and of the conduction band CB inserted. The energy levels for the second dye, Dye2, are inserted in a way corresponding to the first dye, 30 whereby HOMO2 represents the lower level and LUMO2 represents the higher level. The electron transport after photo-excitation with photon energies  $h\nu_1$  and  $h\nu_2$  are indicated with electrons 'e', and by direction arrows placed adjacent 'e'.

In Figure 4b there is shown schematically the spectral light absorption in the first dye, Dye1, 35 and in the second dye, Dye2, as well as in the two semi-conductor materials SC1 and SC2, in

this exemplifying embodiment of the TDSC. Note that SC2 also has its absorption in the UV range.

In the same way Figure 5a shows a corresponding cross section through a TDSC. Figure 5a is  
5 essentially the same as Figure 4a, but with an altered working electrode WE2. SC2 constitutes a nano-structured porous semi-conductor oxide with a long band-gap, and with the levels of the valence band VB and the conduction band CB inserted. The electron transport after photo-excitation with photon energies  $h\nu_1$  and  $h\nu_2$  are indicated with electrons 'e', and by direction arrows placed adjacent 'e'. The second dye and SC2 cooperate for increased photo current in  
10 WE2.

Figure 5b shows schematically, corresponding to figure 4b, the spectral light absorption in the first dye, Dye1, and in the second dye, Dye2, as well as in the semi-conductor materials SC1 and SC2, in this other embodiment of the TDSC according to the invention. Note that SC2  
15 now has its absorption in the visible and/or infra red range.

If both WE1 and WE2 are comprised of porous nano-structured films, two variants can be distinguished (See I and II below). Alternatively the porous film can be grown directly outwards from the underlying conducting substrate. This could have manufacturing  
20 technological advantages, since the film can be made at a low temperature. Cheap substrates of plastics will then become possible to use.

I. The material in the particles in WE2 are comprised of a semi-conductor having a large band-gap (3 eV or higher), e.g. zink selenide (ZnSe), silicon carbide (SiC) or some other  
25 semi-conductor with a high band-gap, which in order to become photo-active must be dye sensitized. The principle is illustrated in Figures 4a and 4b.

II. The material in the particles in WE2 are comprised of a semi-conductor having a band-gap which in itself has an efficient absorption in the visible and/or infra red spectral range. The  
30 principle is illustrated in Figures 5a and 5b, and the function of the two variants are describe in detail below.

I. If WE2 is a porous nano-structured semi-conductor with a large band-gap, the intrinsic absorption of which is in the UV-range, WE2 must be dye sensitized in order that the light  
35 absorption of the electrode also take place in the visible and/or infra red range. Further, it is

- necessary that the energy levels of the second dye is correctly tuned against the energy levels in WE2, such that the HOMO level of the second dye is below VB of the semi-conductor material in WE2. Semi-conductor material in WE2 can advantageously be p-doped. The other energy levels of the dye sensitized electrodes WE1 and WE2 must be tuned against the redox-couple that is active in the electrolyte. I.e., the energy level of the redox-couple must be below the LUMO level of the second dye, and above the HOMO level of the first dye. The principle for this type of cell in energetic terms is given in figure 4a. A schematic drawing of the spectral distribution of the absorption in a solar cell is given in Figure 4b.
- 5
- 10 The most advantageous angle of incidence for sun light in this example is given in Figure 3. Since the TDSC cell involves two separate but coupled photon processes, it is essential for obtaining a high efficiency that the light absorption is adapted such that equal amounts of photons are absorbed in WE1 and WE2, respectively. The validity of the requirement for equal numbers of absorbed photons at WE1 and WE2, respectively, is most easily understood
- 15 if it is assumed that there no losses whatsoever. In reality this condition is valid only if the losses of charge carriers during the transport thereof after respective photo-excitation are equally large. If the losses are different the TDSC device will be optimized with regard to this.
- 20 WE1 functions in principle in the same way as previously described under the heading "Background of the Invention": the first dye is selected such that the electron injection into the electrode material WE1 is so fast as possible, and such that the red-form (Red) of the redox-couple will replace the injected electron as fast as possible. WE2 is characterized in that the second dye should have a long lived excited state, i.e. the electron should live long in the
- 25 sLUMO level of the second dye molecule. This is achieved most easily if the second dye has a long lived triplet state, into which a singlet state will be quantitatively transformed after the photon energy has been absorbed in the second dye. Long life of the excited state is necessary in order that the second dye molecule will have time enough to donate its electron to the oxo form (Ox) of the redox-couple.
- 30 A complete cycle following the photon processes in a TDSC occurs according to the following scheme:

At the WE1:

- A photon is absorbed in the first dye, whereby an electron is raised in energy from the first HOMO 1 level to the first LUMO 1 level
  - The electron is injected in SC1
  - Red donates an electron to the LUMO1 level in the photo-oxidized first dye
- 5 - The electron in SC1 reaches the back contact and passes through the external lead via an ohmic back contact to the VB of the nano-structured SC2 material

At WE2

- 10 - A photon is absorbed in the first dye, whereby an electron is raised in energy from the second HOMO level to the second LUMO2 level
- The electron in the second LUMO2 reduces Ox to Red
  - An electron is transferred from the VB of SC2 to the HOMO2 level of the second dye
- 15 The maximum photo voltage in this type of TDSC is given by  $U_{OC}$  in Figure 4a.

II. If WE2 is a semi-conductor with a band-gap having its absorption in the visible and/or infra red region, it can constitute a photo-active electrode, if its absorption spectrum and absorption is correctly tuned against the dye sensitized electrode WE1, and its other energy levels are tuned against the active redox-couple in the electrolyte, and the energy levels in WE1, although it is not dye sensitized. The material in the particles would then be comprised of some (intrinsic or p-doped) semi-conductor, e.g. GaAs, CdS, CdSe, CuInSe<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, which in themselves are capable of absorbing light in the visible and/or infra red range. The principle in energetic terms for this type of cell is given in Figure 5a. A schematic drawing of the spectral distribution of the absorption for a solar cell of this type is shown in Figure 5b.

20 Also here it is essential that the light absorption is adapted such that an equal number of photons are absorbed in WE1 and in WE2, respectively. However, also in this type of cell the light absorption in WE2 can be amplified by adsorbing a dye on the surface of the electrode.

25 The discussion under I above regarding the mutual relation between energy levels, is applicable also in this type of solar cell.

30 Under II above a case was discussed wherein WE1 is dye sensitized and WE2 is a semi-conductor having a band-gap with absorption in the visible and/or infra red range. Of course it is possible to permute this condition, such that WE2 is the dye sensitized electrode and WE1 is a semi-conductor having a band-gap in the visible and/or infra red range.

Independently of the type of tandem cell (I or II), a larger or smaller amount of dye can be adsorbed in a mono-layer to the inner surface of the electrode material, and in this way it is possible to tune WE2 against WE1 such that the desired balance between the number of  
5 absorbed photons in the two photo-electrodes is obtained. The maximum value of the photo voltage  $U_{OC}$  TDSC is the difference between the energy levels VB in WWE2 and CB in WE1. One can thus expect a substantially higher photo voltage from a TDSC device compared to a prior art DSC device.

10 EXAMPLE 1:

In this Example a TDSC cell has a WE1 electrode which is an electrode made of porous titanium dioxide ( $TiO_2$ ), dyed with a ruthenium dye, comprised of a ruthenium bis-pyridine complex of a known type. However, a large number of dyes are conceivable. Instead of a dye  
15 a very thin layer of a semi-conductor can be used. Such a semi-conductor is of course assumed to absorb in the visible and infra red part of the light spectrum. Functional groups binding to the titanium dioxide surface (e.g. phosphonyl groups or carboxyl groups  $-COOH$ ), are covalently bound to at least one of the bipyridine ligands, according to known techniques, in order to obtain an efficient absorption of the dye to the particles of the titanium dioxide.

20 The electrode WE2 is comprised of porous, nano-structured, p-doped silicon carbide (SiC), which has been dye sensitized with a dye (B)  $Ru(bpy)(Bpz)_2$ , wherein bpy is bipyridine ligand and bpz is a bi(1,4)diazine ligand rutenium complex [Inorg. Chem. 22, (1983), 224], the HOMO level of which is below the valence band of the silicon carbide. For the electrolyte e.g. an iodine/iodide system ( $I_2/I^-$ ) is used in the solvent acetonitril or some other  
25 correspondingly polar solvent. The total content of  $I_2$  is typically 50 mM and the total content of  $I^-$  is typically 1,0 M.

EXAMPLE 2:

30 The cell in this example is in all details as in the embodiment 1, but with the difference that the silicon carbide SiC has been replaced by zink selenide (ZnSe).

- EXAMPLE 3:

The cell in this example is in all details as in the embodiment 1, but with the difference that the silicon carbide SiC has been replaced by nano-particles of  $\text{Fe}_2\text{O}_3$ .

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EXAMPLE 4:

The cell in this example is in all details as in the embodiment 3, but with the addition that  
10 nano-crystalline rods of  $\text{Fe}_2\text{O}_3$  in the  $\mu\text{m}$  size constitute the active porous nano-structure in WE2.

EXAMPLE 5:

The cell in this example is in all details as in the embodiment 4, with the addition the nano-  
15 crystalline rods of  $\text{Fe}_2\text{O}_3$  are anisotropically arranged with an orientation at right angles to the plane of the substrate.

EXAMPLE 6:

20 The cell in this example is in all details as in the embodiments 3, 4 and 5, but the inner surface of the  $\text{Fe}_2\text{O}_3$  film is provided with a mono-layer of dye sensitizing substance.

EXAMPLE 7:

25 An electrode having a “p-type behavior” was made from a transparent substrate in the form of a glass plate having an electrically conducting coating, on which had been deposited nano-structured NiO. The average diameter of the particles were 10-20 nm. They were applied onto the glass substrate with a doctor blade technique, which is type of gel coat technique. A  
30 spacer (a few tens  $\mu\text{m}$  thick) was glued in parallel along two edges of the conducting glass. A viscous solution containing the colloidal nano-particles was added. Excess solution was raked off. When the film had dried the spacer strips were removed and the film was sintered at about 500°C.

NiO is known as a semi-conductor with a large band-gap (3,6 – 4,0 eV) and has a tendency to  
35 exhibit “p-type behavior” as prepared.

**EXAMPLE 8:**

The electrode from Example 6 was dye sensitized by coating it with tetrakis(4-carboxyphenyl)porphyrin (TPPC). Also this electrode (in the same electrolyte) exhibits p-type behavior on illumination with 1000W solar simulator (lamp: Xenon). This is illustrated in Figure 6.

**EXAMPLE 9**

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The electrode from Example 8 was mounted as photo electrodes in a measurement set-up with a Pt electrode as a counter electrode.

Figure 6b shows the iV characteristics for this nano-structured NiO electrode. The photo voltage is about 110 mV.

In figure 6a is shown the iV characteristics for a TiO<sub>2</sub> electrode that has been sensitized with the dye N3 [(*cis*-bis(4,4'-dicarboxy-2,2'-bipyridine)-bis(isothiocyanato)ruthenium(II)]. A photo voltage ("open circuit") of about 450 mV is obtained.

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**EXAMPLE 10:**

The electrodes tested separately in Example 9, are mounted in a tandem cell such that the NiO electrode functions as the cathode, and the TiO<sub>2</sub> electrode as the anode.

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The iV characteristics are shown in Figure 6c. It is clear that the photo voltage on illumination is additive such that the tandem cell obtains a higher photo voltage than the each electrode by itself.

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Although this photo voltage has not been optimized, it should be obvious that the invention is workable. Photo voltages of at least 1,5 V, preferably about 2,0 V are fully achievable using this principle. Other dyes are also conceivable, e.g. Erythrosin B. Further variations of the embodiments can be achieved by the skilled man by employing prior art teachings. Since each component in each individual electrode WE1 and WE2, as well as the components in the electrolyte can be varied, the number of possible embodiments is large. Instead of TiO<sub>2</sub> in

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- WE1, ZnO could e.g. be used. Instead of ruthenium polypyridine complexes, other dye categories could be used, e.g. porphyrins and phtalocyanines. Instead of the iodine-iodide system, other redox-systems could be used. Also the solvent for the electrolyte and the salts therein can be varied. The embodiments of Examples 1-10 above therefore should only be  
5 regarded as a few examples of different embodiments of a tandem cell according to the present invention. The TDSC device however, is always characterized by the general properties summarized under the description of the technology of the invention.

- CLAIMS:

1. A photo-voltaic cell, comprising a first and a second nano-structured working electrode (WE1, WE2) and an electrolyte located between said electrodes and comprising a redox-couple, wherein  
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the working electrodes have an energy level structure such that electrons are excitable from a level which is below the redox potential of the redox-couple in the electrolyte to a level which is above the redox potential, and wherein

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at least one of the working electrodes (WE1) is a dye sensitized, nano-structured electrode.

- 15 2. The cell according to claim 1, wherein both the first and the second working electrodes are dye sensitized, nano-structured electrodes.

3. The cell according to claim 1, wherein the second working electrode is a nano-structured semi-conductor having a band-gap corresponding to absorption in the visible and/or infra red spectral region.

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4. The cell according to claim 1, wherein the second working electrode is a dye sensitized, nano-structured electrode.

- 25 5. The cell according to claim 2, wherein the second working electrode is a semi-conductor having a large band-gap, e.g. larger than 3 eV.

6. The cell according to claim 5, wherein the second working electrode is selected from NiO, SiC, ZnSe and similar semi-conductors with a large band-gap.

- 30 7. The cell according to claim 1, characterized in that the material in the photo-active working electrode (WE2) is comprised of particles of a material constituting a semi-conductor having a small band-gap, which itself has an efficient light absorption in the visible and/or infra red spectral region.

8. The cell according to claim 7, characterized in that the semi-conductor in the second photo-active working electrode (WE2), having absorption in the visible and/or infra red spectral region, by dye sensitization has its absorption spectrum tuned against the dye sensitized first working electrode (WE1), and in that its energy levels are tuned against the  
5 active redox-couple in the electrolyte.

9. The cell according to claim 1, characterized in that the electrolyte is an iodide-iodine system in a polar solvent, e.g. acetonitril or the like.

10 10. The cell according to claim 1, characterized in that the material in the second photo-active working electrode (WE2) is comprised of porous, nano-structured, p-doped silicon carbide (SiC), which has been dye sensitized with a ruthenium complex of the composition Ru(bpy)(Bpz)<sub>2</sub>, wherein bpy is bipyridine ligand and bpz is a bi(1,4)diazine ligand, the HOMO level of which is below the valence band of the silicon carbide.  
15

11. The cell according to claim 1, characterized in that the material in the second photo-active working electrode (WE2) is comprised of zink selenide, which has been dye sensitized with a ruthenium complex of the composition Ru(bpy)(Bpz)<sub>2</sub>, wherein bpy is bipyridine ligand and bpz is a bi(1,4)diazine ligand, whereby the HOMO level of the ruthenium complex  
20 is below the valence band of the zink selenide.

12. The cell according to claim 1, characterized in that the material in the second photo-active working electrode (WE2) is comprised of nano-particles of Fe<sub>2</sub>O<sub>3</sub>, which has been dye sensitized with a ruthenium complex of the composition Ru(bpy)(Bpz)<sub>2</sub>, wherein bpy is  
25 bipyridine ligand and bpz is a bi(1,4)diazine ligand, whereby the HOMO level of the ruthenium complex is below the valence band of Fe<sub>2</sub>O<sub>3</sub>.

13. The cell according to claim 1, characterized in that the material in the second photo-active working electrode (WE2) is comprised of nano-crystalline rods of Fe<sub>2</sub>O<sub>3</sub>, the length of  
30 which is in the µm range, which have been dye sensitized with a ruthenium complex of the composition Ru(bpy)(Bpz)<sub>2</sub>, wherein bpy is bipyridine ligand and bpz is a bi(1,4)diazine ligand, whereby the HOMO level of the ruthenium complex is below the valence band of Fe<sub>2</sub>O<sub>3</sub>.

14. The cell according to claim 13, wherein the nano-crystalline rods of  $\text{Fe}_2\text{O}_3$  are anisotropically arranged with an orientation at right angles to the plane of the substrate.
15. The cell according to claim 1, wherein the first photo-active working electrode is a nano-structured  $\text{TiO}_2$  electrode which has been sensitized with a ruthenium bispyridine complex, and wherein the second photo-active working electrode is a nano-structured  $\text{NiO}$  electrode which has been sensitized with tetrakis(4-carboxy)porphyrin (TPPC).  
5
16. The cell according to any preceding claim, wherein the dye/dyes used are selected from Erythrosin B, ((cis-bis(4,4'-dicarboxy-2,2'-bipyridine)-bis(isothiocyanato)ruthenium(II))  
10 (N3), tetrakis(4-carboxy)porphyrin (TPPC) 1.

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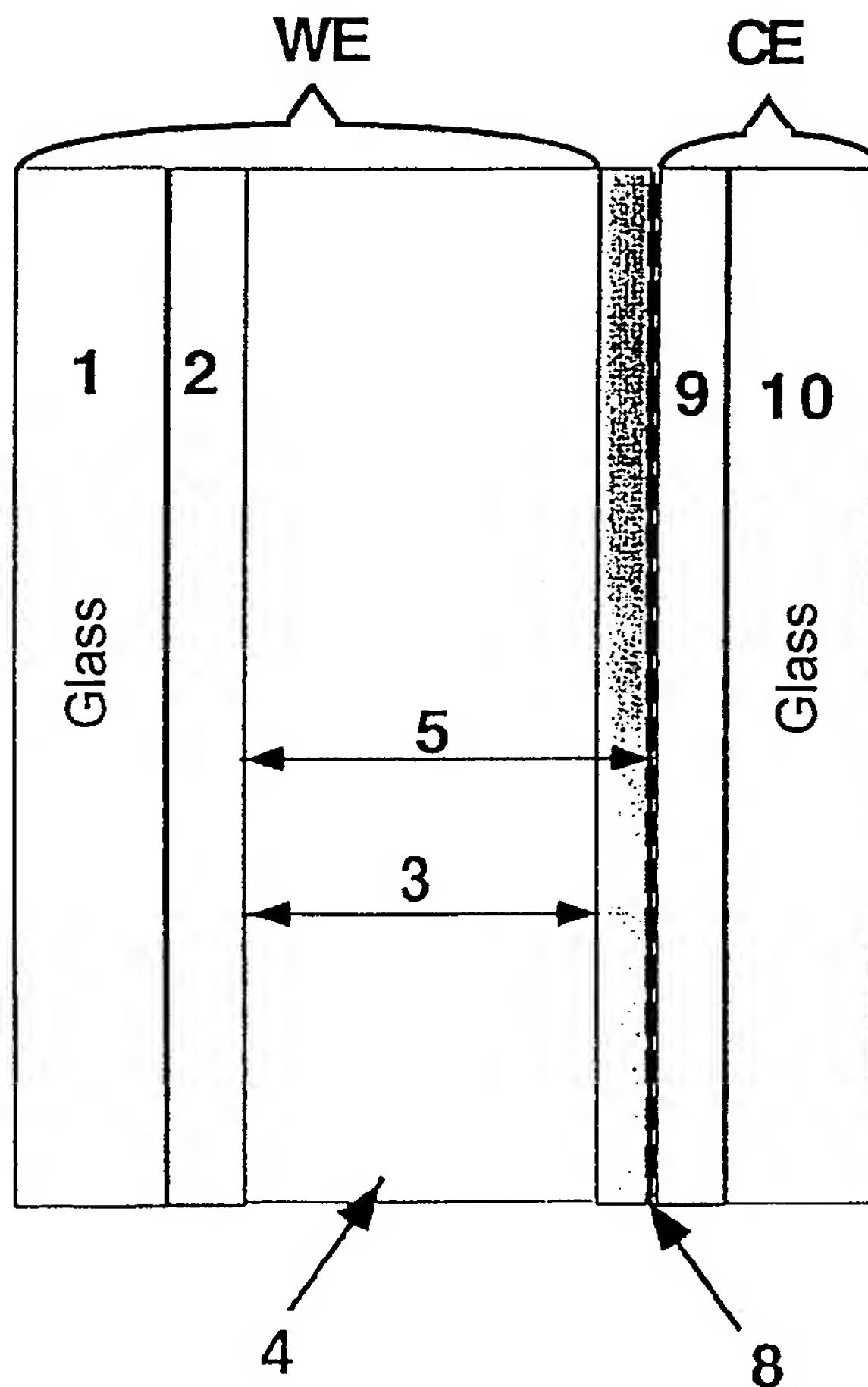


Fig. 1

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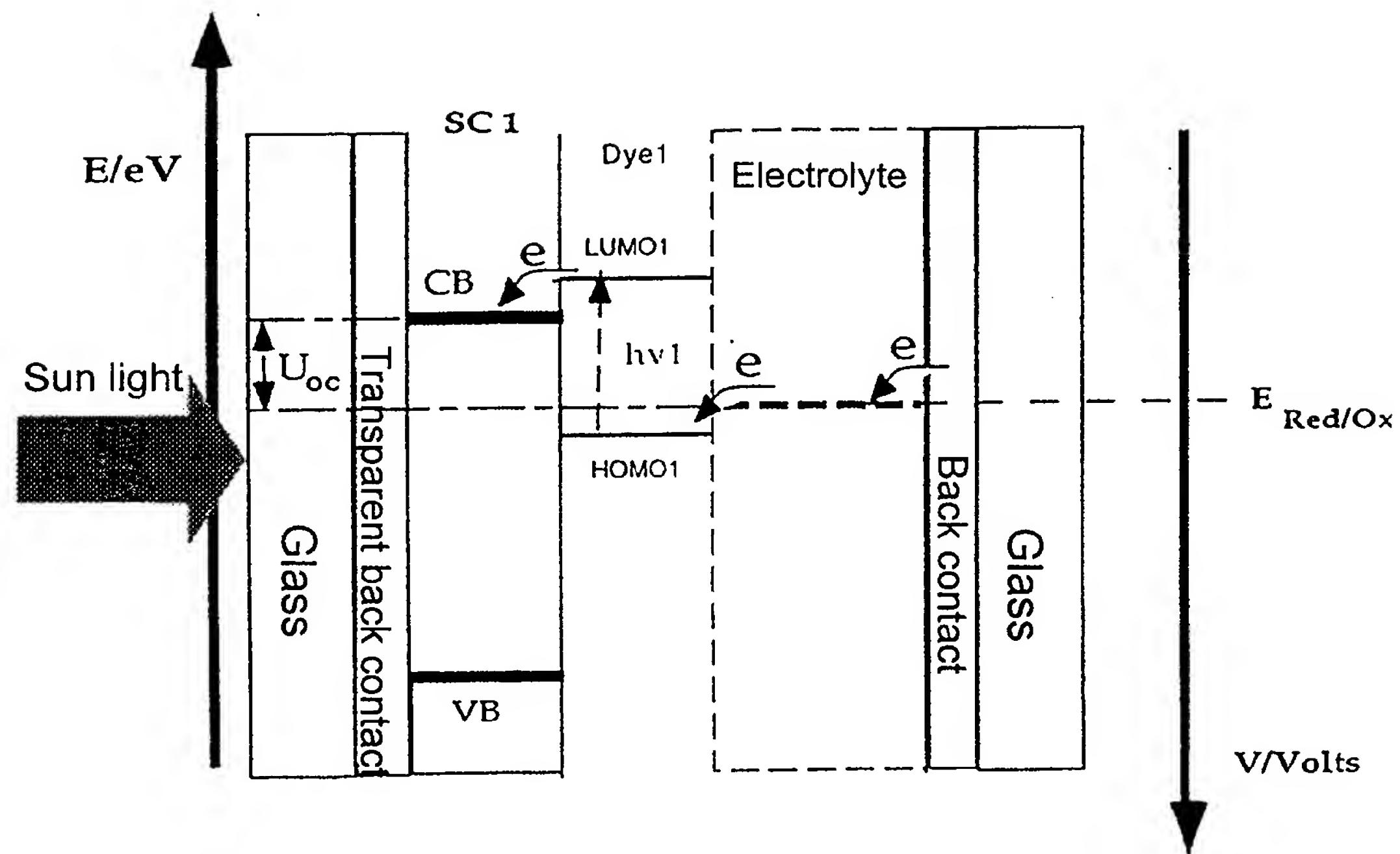


Fig. 2a

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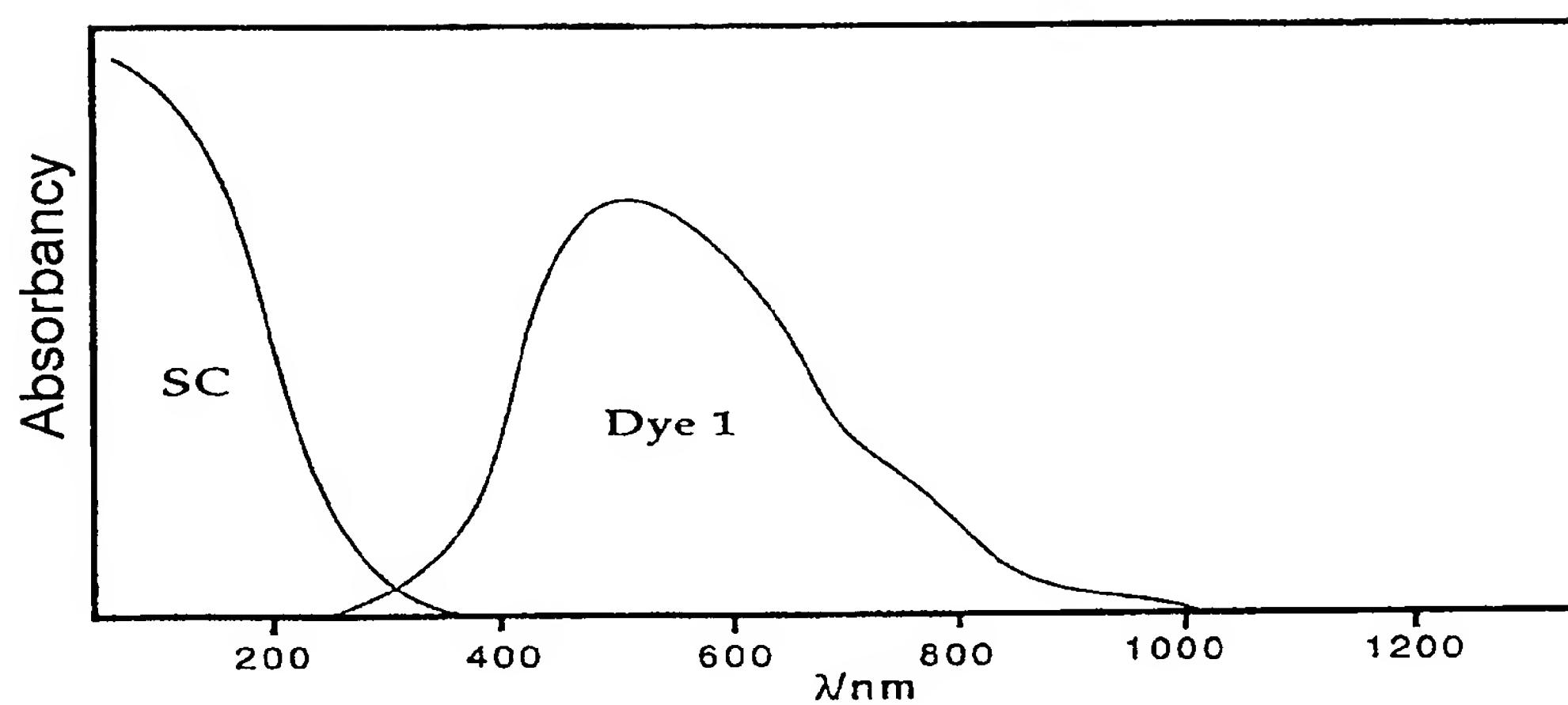


Fig. 2b

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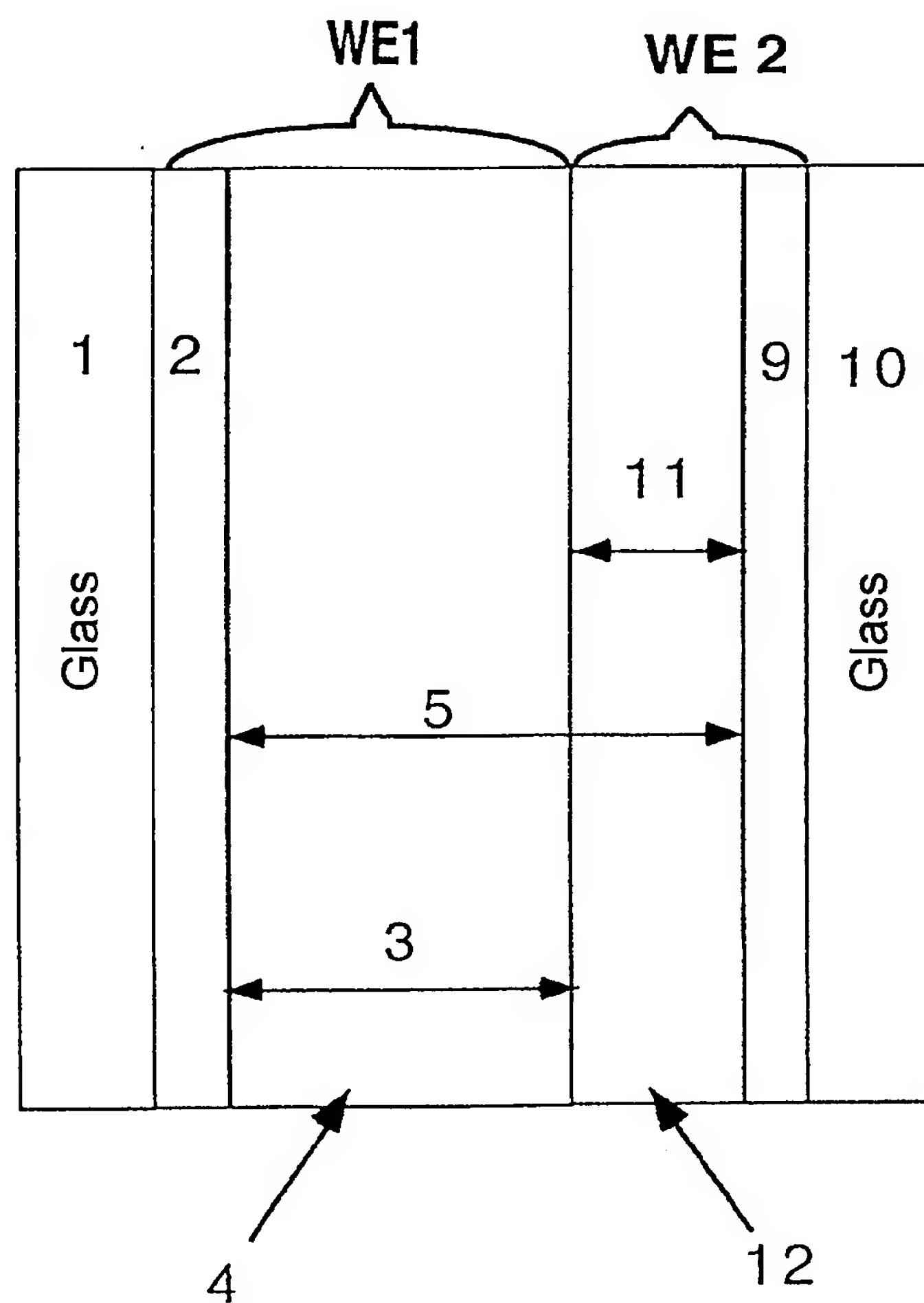


Fig. 3

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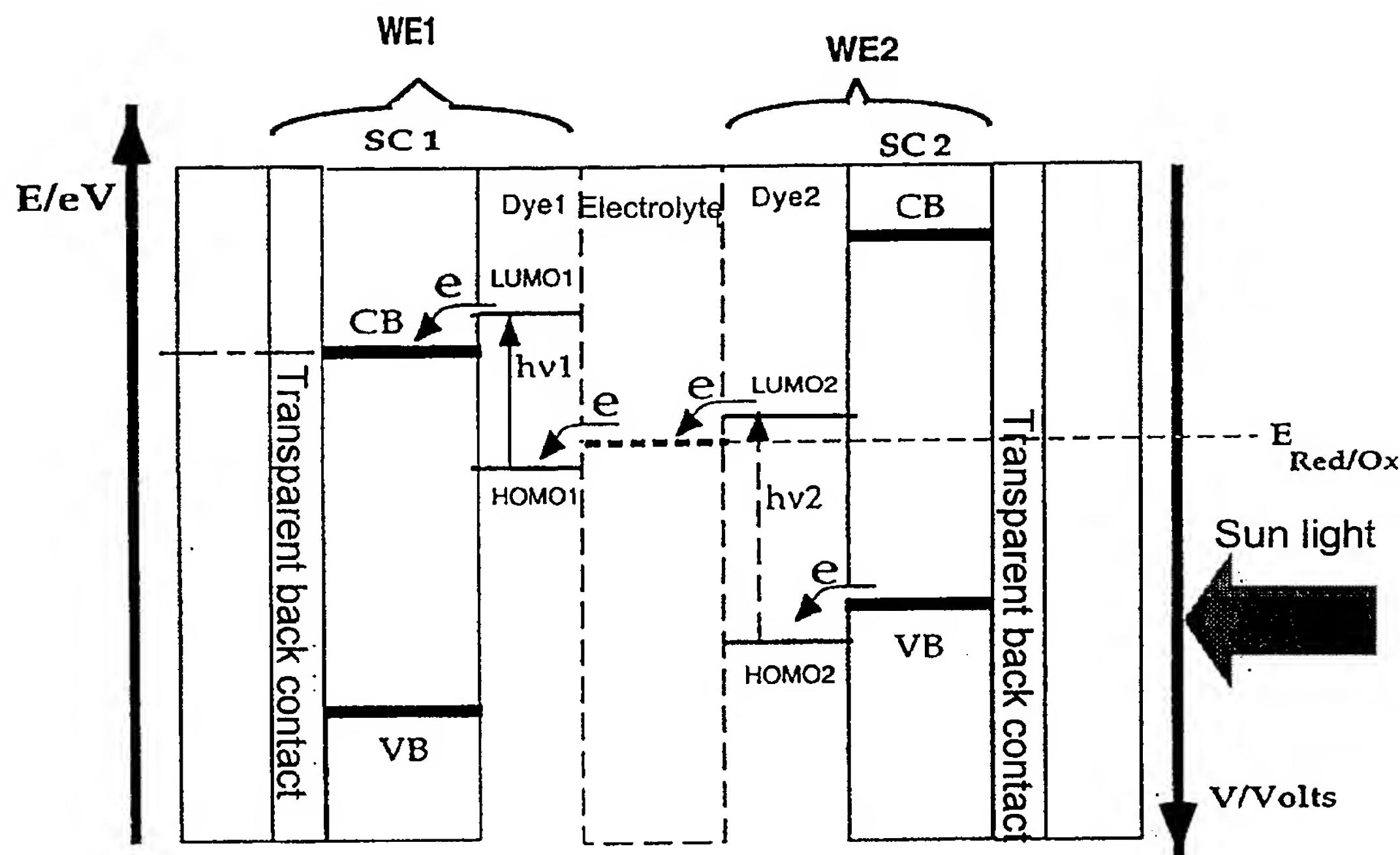


Fig. 4a

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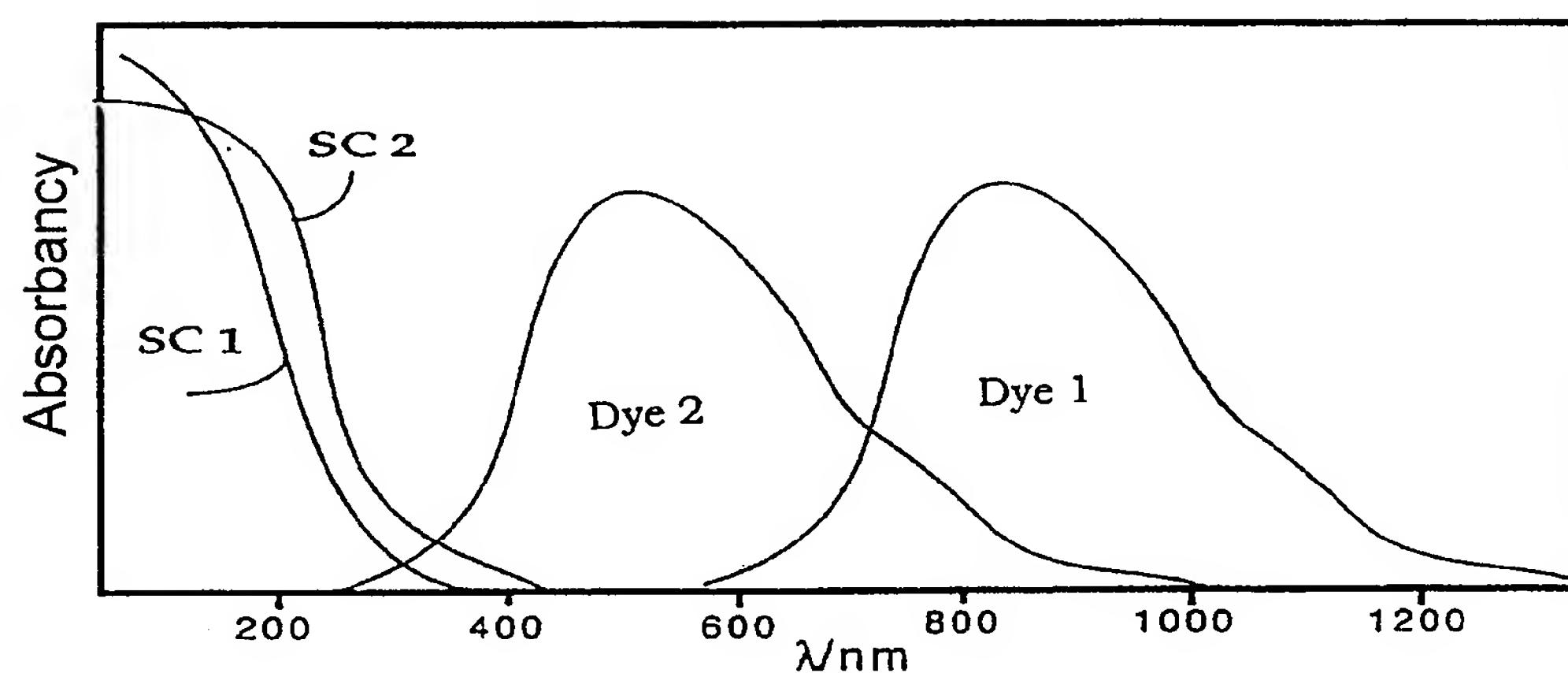


Fig. 4b

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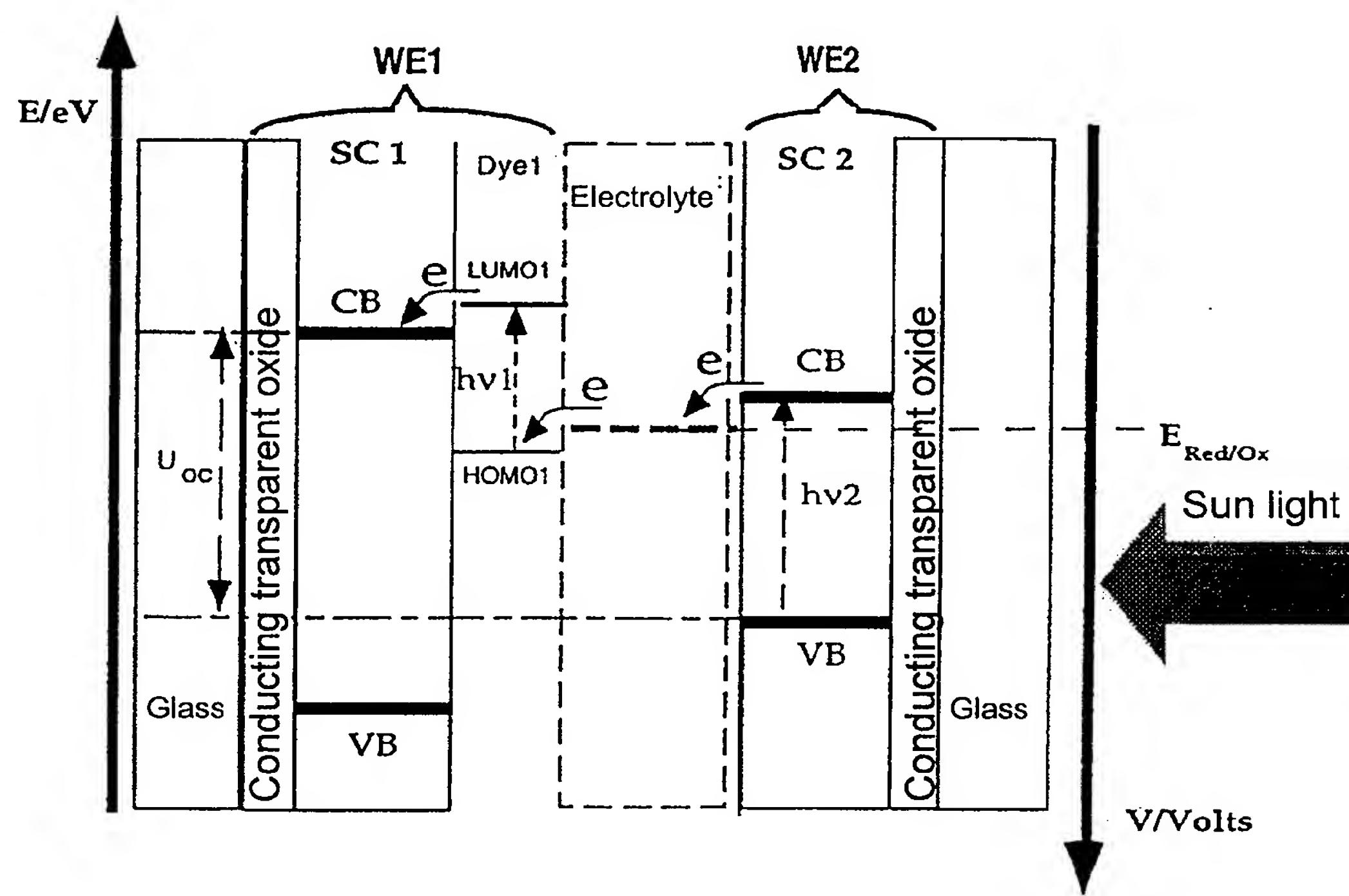


Fig. 5a

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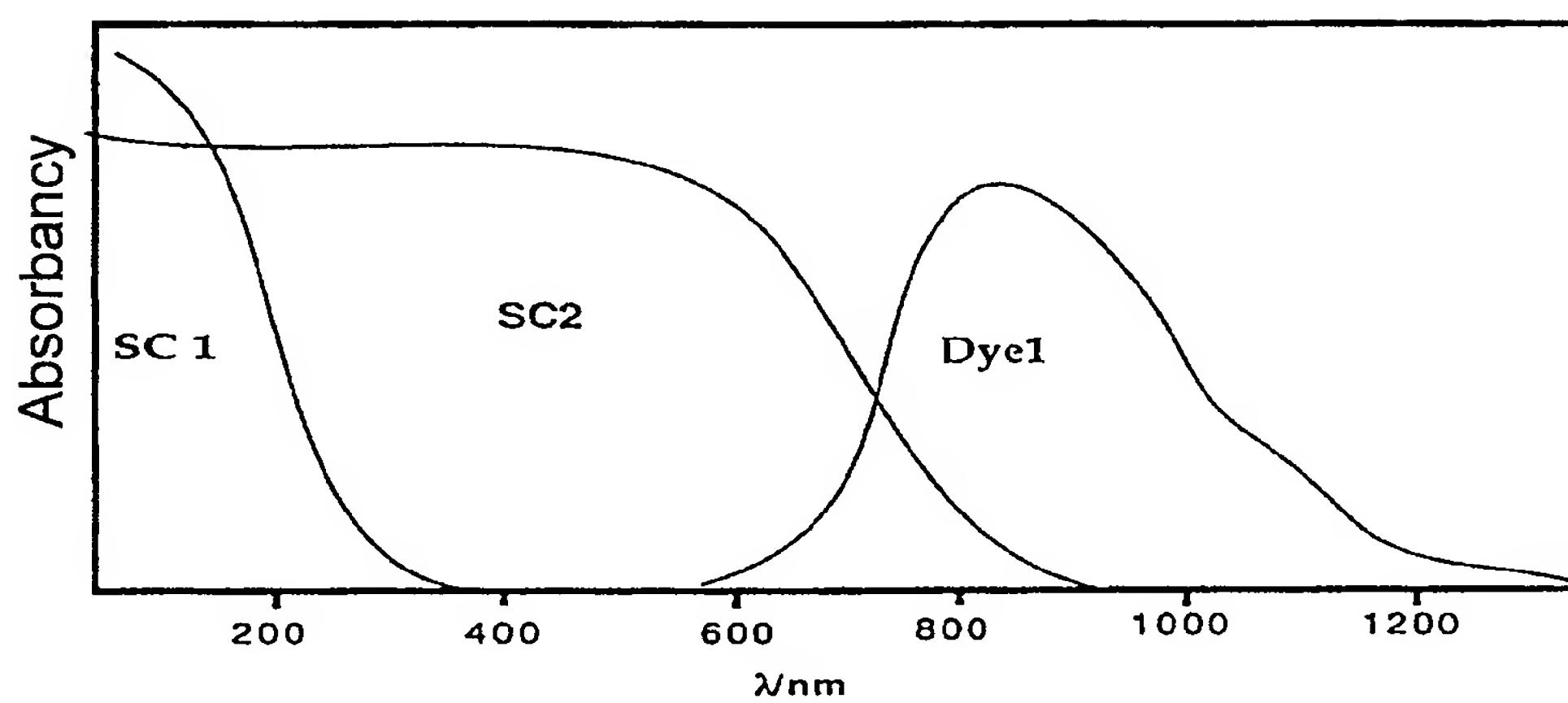


Fig. 5b

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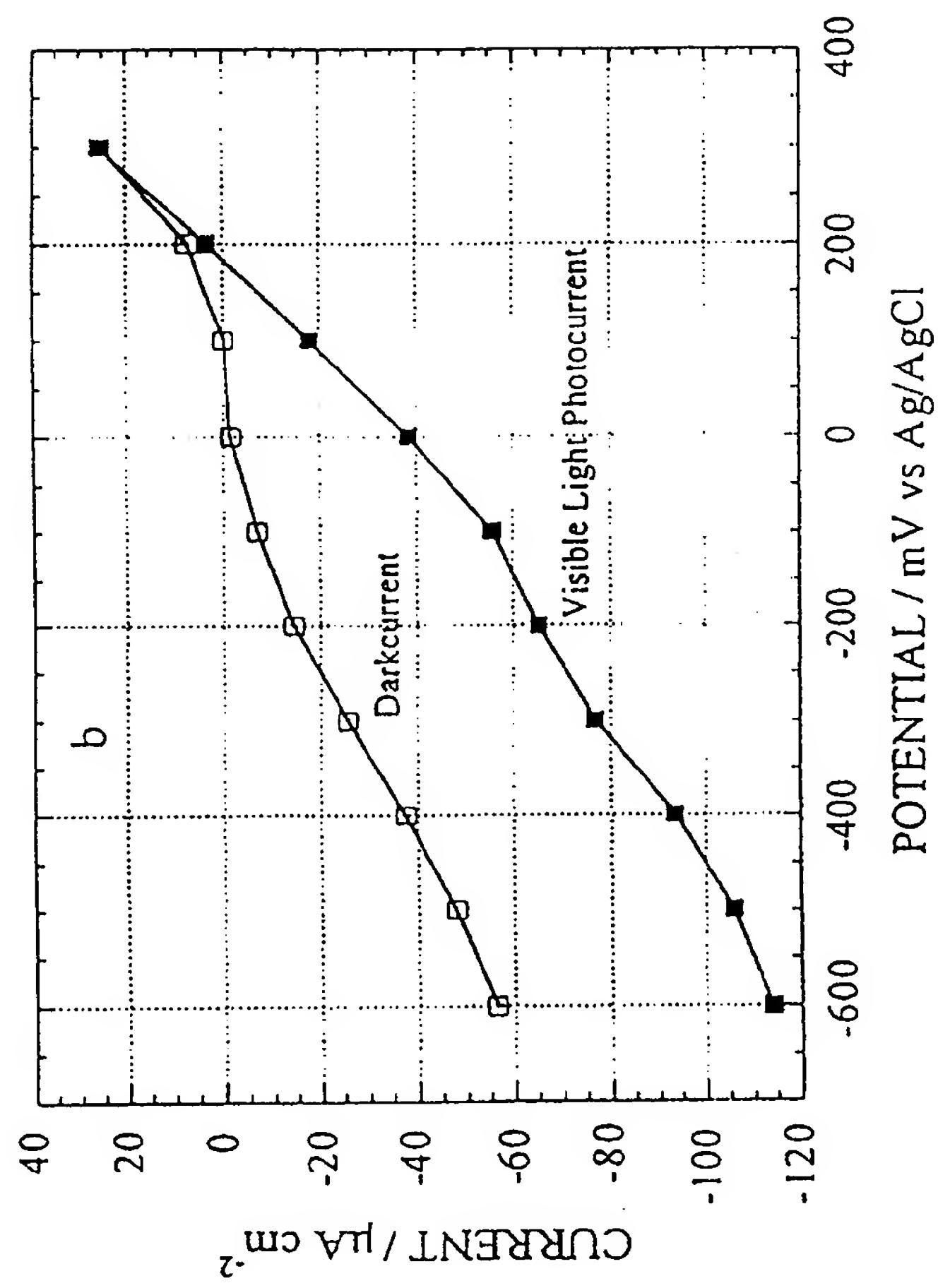


Fig. 6

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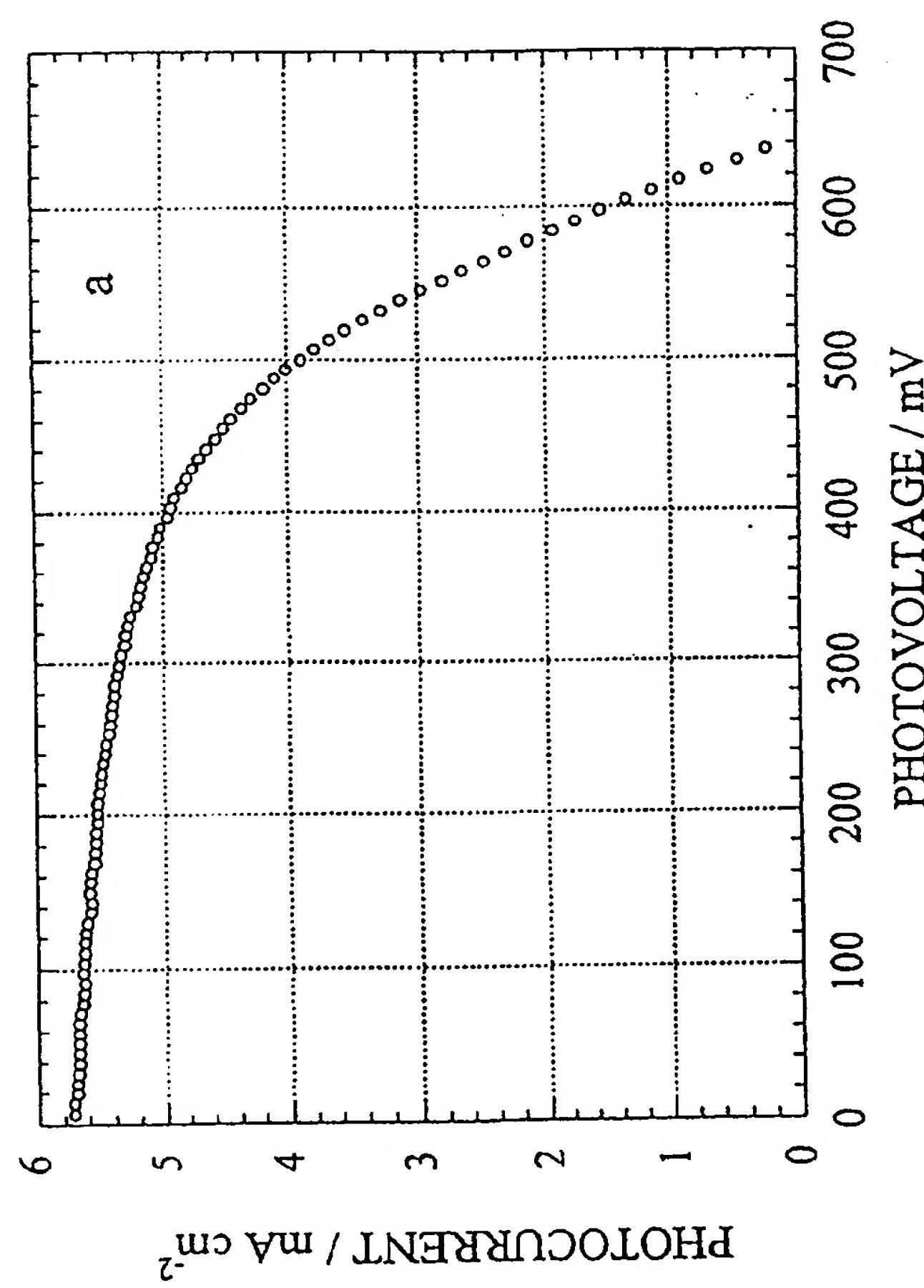


Fig. 7a

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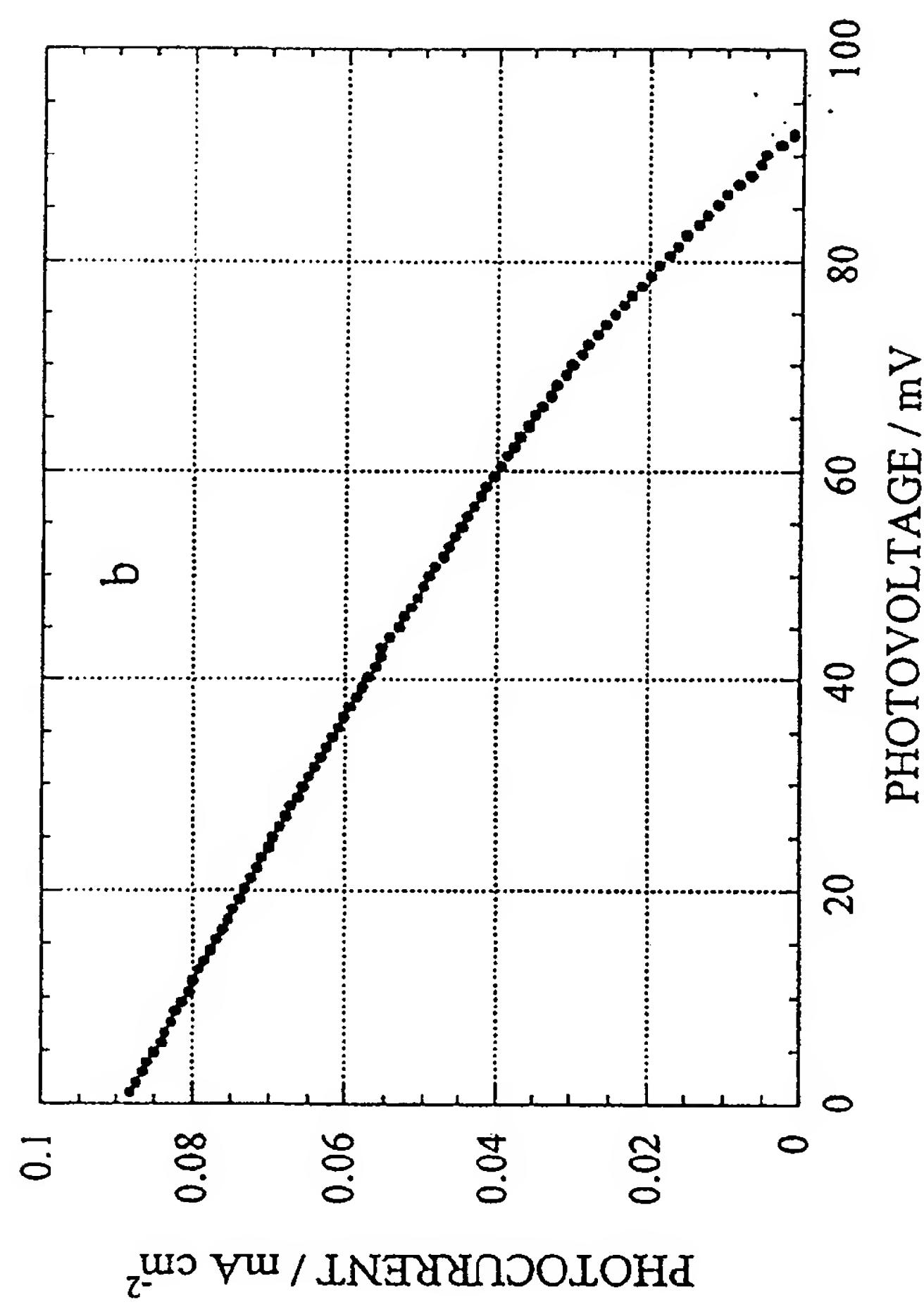


Fig. 7b

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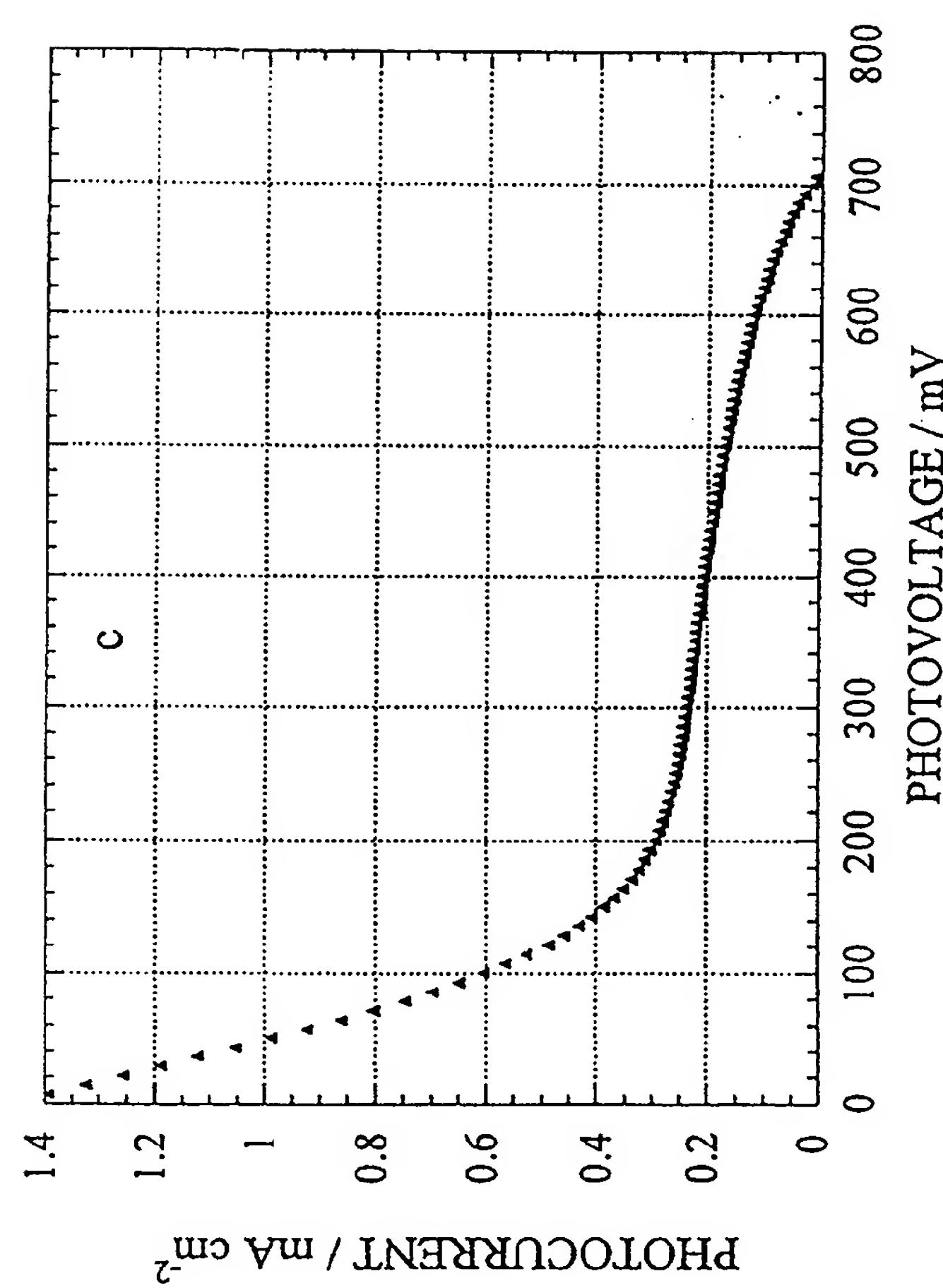


Fig. 7c

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/SE 99/00290

## A. CLASSIFICATION OF SUBJECT MATTER

**IPC6: H01L 31/04 // H01G 9/20, H01M 14/00**

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

**IPC6: H01L, H01G, H01M**

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

**SE, DK, FI, NO classes as above**

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

**WPI, EPDOC, PAJ**

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5084365 A (MICHAEL GRATZEL ET AL), 28 January 1992 (28.01.92), column 4, line 7 - line 25, figure 1  --	1-16
A	US 4416959 A (TERJE SKOTHEIM), 22 November 1983 (22.11.83), column 5, line 48 - column 6, line 2, figure 7  -- -----	1-16

Further documents are listed in the continuation of Box C.

See patent family annex.

\* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

27 August 1999

Date of mailing of the international search report

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

02/08/99

International application No.
PCT/SE 99/00290

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